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Structural Analysis of $Im3m$ Phase of BABH- n by Maximum Entropy Method

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BABH- n は剛直なコアとその両側にアルキル鎖をもち、鎖長に応じて異なる対称性のキュービック液晶相 ($Ia3d$ 相, $Im3m$ 相) を発現する。 $Ia3d$ 相の内部構造は小角 X 線散乱の散乱強度の鎖長依存性を利用して決定されたが、 $Im3m$ 相では同じ手法による構造決定はできない。 本研究では、少数のピークから最も確からしい電子密度分布を推定する最大エントロピー法を $Im3m$ 相に適用した。

1 Introduction

Cubic phase is a kind of liquid crystal having three dimensional periodicity. The title compound, 1,2-bis(4'- n -alkoxybenzoyl)hydrazine (BABH- n , Fig. 1), forms such cubic phases [1]. The space group of the cubic phase depends on the length of the alkyl chains: $Ia3d$ cubic phase ($Ia3d$ -Cub phase) appears in $5 \leq n \leq 13$ and $16 \leq n$ (≤ 22 at present) and $Im3m$ one ($Im3m$ -Cub phase) in $13 \leq n \leq 16$.

It is known that the basic structure of $Ia3d$ -Cub phase is triply periodic minimal surface Gyroid. The internal structure of the Gyroid was determined recently by examining the alkyl chain dependence of small-angle X-ray scattering (SAXS) on BABH- n [2]. The alkyl chains of BABH- n molecules locate on the Gyroid surface and those cores form a jungle gym-like aggregation. On the other hand, the same method failed to locate which part of molecules on the surface or rod for $Im3m$ -Cub phase ($13 \leq n \leq 16$). The internal structure of $Im3m$ -cubic phase, thus, has not been clarified yet.

The change in symmetry of cubic phases is found not only in BABH- n but in another compound which shares characteristics in molecular structure (rigid core and flexible chains on both ends). Therefore, elucidating internal structure of $Im3m$ -Cub phase of BABH- n is expected to wider applicability.

Diffraction crystallography (SAXS in this case) is a standard method to determine experimentally the periodic structures. The number of diffractions from the cubic phases is however about ten due to highly disordered nature of the phase. Besides, the SAXS data is completely determined by the contrast of electron density, originating from difference in electron density between the core and the alkyl chain of BABH- n molecule. This was the reason why the straightforward analysis could not be applicable but the chain-length dependence of the ratio of the scattering intensities was used for the $Ia3d$ phase [2]. For the $Im3m$ phase, the basic structure itself is under debate. The limited number of the SAXS peaks may generate negative density and ghost peaks in the conventional Fourier synthesis of the electron density. To avoid

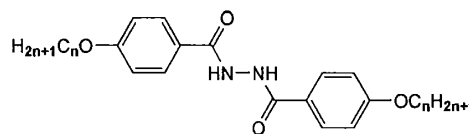


Fig. 1: Structural Formula of BABH- n

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them, we adopted the so-called Maximum Entropy Method (MEM) to the data. The MEM provides the most probable distribution of the electron density from the limited diffraction data.

2 Calculation

In the MEM, most ambiguous electron density distribution that satisfies constraints is calculated. Ambiguity is represented as information entropy S which is related to density distribution. Constraint C is that results of calculation match observation within error. The both quantities are given by ;

$$S = - \sum_{\mathbf{x}} \rho'(\mathbf{x}) \ln \frac{\rho'(\mathbf{x})}{\tau'(\mathbf{x})}, \quad C = \frac{1}{N} \sum_{\mathbf{k}} \frac{|F_{\text{cal}}(\mathbf{k}) - F_{\text{obs}}(\mathbf{k})|^2}{\sigma^2(\mathbf{k})} \approx 1,$$

where $\rho'(\mathbf{x})$ is electron density, $\tau'(\mathbf{x})$ initial electron density, $F(\mathbf{k})$ structural factor and $\sigma(\mathbf{k})$ standard deviation. We search for $\rho(\mathbf{x})$ which maximizes the information entropy S self-consistently under the constraint by Lagrange's method of undetermined multipliers.

3 Results and Discussion

Although the structure factors derived from the intensity of the diffraction peaks are needed for the analysis, the SAXS pattern does not provide us "phase" of the structure factors directly. To dissolve the phase problem, we assumed and compared four combinations of the phases of the largest two peaks (321) and (400); (+, +), (−, −), (+, −) and (−, +), respectively. Only the absolute values of the other peaks are taken into consideration by modifying the constraint.

The resultant isosurfaces of the electron density of BABH-13 are shown in Fig. 2. The threshold of the isosurface is an average of the electron density. The four pictures correspond to four phase combinations of the largest two peaks. We will discuss the phase combinations and the internal structure from a view point of the alkyl chain length, leading to the most appropriate internal structure of $Im3m$ -Cub phase of BABH- n .

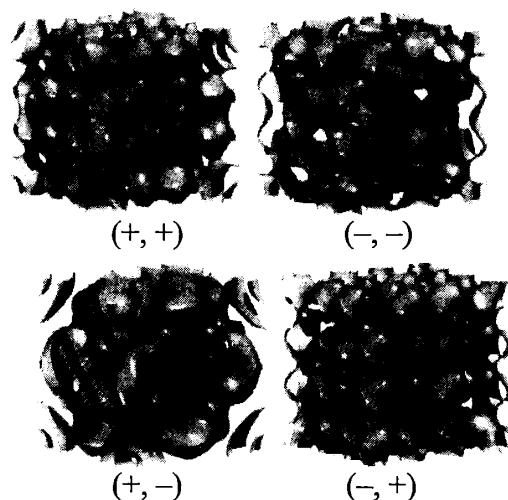


Fig. 2: Electron density map of $Im3m$ -Cub phase of BABH-13. Signs indicate phases of structural factors corresponding to the peaks (321) and (400), respectively.

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